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TITLE: Thin uniform vacuum deposited coatings - using simultaneously evaporated carrier of quartz and boride of silicide

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PATENT-FAMILY:

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BASIC-ABSTRACT:

Vacuum deposited coatings are obtained by simultaneous evaporation of a carrier comprising quartz and a boride and/or silicide together with at least one of Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cs, Cu, Dy, Cr, Eu, Ga, Gd, Ge, Ho, K, La,Li, Lu, Zn, Mg, Mn, Mu, Mo, Nb, Nd, Na, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, Tm, V, W, Y, Yb, Zn, Zr, Ac, Am, Ac, Bc, Cf, Cm, Es, Fm, Fr, Md, Np, No, Pm, Po, Pm, Pa, Ra, Rn or Tc(sic), compounds of those elements, or alloys formed from them. The preferred carrier contains the boride and/or silicide of tungsten. Particular selections of the above metals are claimed for producing coatings having predetermined (a) electrical conductivity, (b) magnetic properties (c) optical properties, (d) radioactive properties (e) photoelectric properties and (f) semiconductive properties. Then uniform coatings may be obtained having desirable combinations of properties.

TITLE-TERMS: THIN UNIFORM VACUUM DEPOSIT COATING SIMULTANEOUS EVAPORATION CARRY QUARTZ BORIDE SILICIDE

DERWENT-CLASS: L03 M13

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(54) IMPROVEMENTS IN OR RELATING TO VACUUM DEPOSITED COATINGS

(71) I, LOTHAR REHFELD, a Citizen of the Federal Republic of Germany, of 7, Struningweg, D-46, Dortmund-Aplerbeck, German Federal Republic, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of producing coatings having various physical properties, on a substrate by vacuum deposition.

In practice many difficulties are encountered when it is desired to produce uniform coatings consisting of only a few molecule layers by means of conventional coating methods. The formation of uniform coatings is generally impeded by the fact that the evaporated molecules do not condense uniformly on each of the surface elements of the carrier or substrate because this condensation is preferred on certain surface elements. Therefore it may be observed that after a relatively short evaporating period a multi-molecule layer evaporation coating will have deposited in certain areas on the substrate whereas no deposition at all will have taken place in other areas. The whole coating will not be formed until a certain time has elapsed, and the formation of the coating is due to lateral growth of the "condensation islands". A continuous uniform evaporation coating may thus only be obtained after a certain amount of substance has been evaporated.

When it is desired to obtain certain physical characteristics such as a predetermined electrical conductivity then a coating produced merely by the evaporation of a physically active material may already have such a thickness that the desired value of the electrical conductivity has already been exceeded.

Our parent Patent Specification No. 1,262,525 describes and claims a method of producing coatings by vacuum deposition which method comprises evaporating onto a substrate quartz, a metal boride or a metal silicide, or mixtures thereof, simultaneously with at least one element or compound.

The present invention provides a method of producing coatings by vacuum deposition which method comprises evaporating onto a substrate a carrier material which comprises quartz and a metal boride and/or a metal silicide simultaneously with at least one of the elements Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Ho, K, La, Li, Lu, In, Ma, Mn, Mu, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, Tm, V, W, Y, Yb, Zn, Zr, Ac, Am, At, Bc, Cf, Cm, Es, Fm, Fr, Md, Np, No, Pn, Po, Pm, Pa, Ra, Rn or Tc or compounds of the said elements, or alloys formed from the above elements.

The metal boride or metal silicide is preferably tungsten boride or tungsten silicide. The concentration of the elements or compounds thereof may vary within a range of from less than 1 per cent up to 99 per cent of the total material present in the coating. The method of the invention enables coatings to be produced having two or more physical and/or chemical properties. A coating produced in accordance with the present invention may have electrically conductive, magnetic, optical, radioactive, photoconductive or semiconductive properties, and depending upon the selective process steps the coating may possess one or more of these properties.

In carrying out the method of the invention one or more of the elements listed above, or compounds, or alloys of the said elements may be thoroughly intermixed in desired proportions with the quartz and the metal boride and/or the metal silicide. The mixing step may be carried out in any conventional manner known to the one skilled in the art. Then this mixture is introduced into a vacuum chamber and evaporated therein onto the substrate under well-known conditions whereby a coating is produced on the substrate.

According to another procedure the quartz and the metal boride and/or metal silicide and one or more of the elements listed above, or compounds or alloys of the

said elements may be evaporated simultaneously but separately to produce a coating on a substrate.

The coatings produced by the method of the present invention possess to a great extent the mechanical properties of the base substance and are therefore particularly wear-resistant and possess a relatively excellent temperature stability.

To obtain a predetermined electrical conductivity of the coating one or more of the following elements may be evaporated onto the substrate Al, Au, Be, Cd, Co, Cu, In, Mg, Mu, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Sm, Sn, Sr, Ta, Th, Tl, Tm, V, W, Y, Yb, Zn, and Zr and/or oxygen compounds of one or more of these elements whereby the oxygen compound deposited on the substrate is of a lower degree of oxidation than the substance employed, and/or alloys formed of the above elements.

By suitable selection of the degree of doping, electrical resistors may be obtained having resistance values within a very wide range.

To obtain predetermined magnetic properties of the coating one or more of the following elements may be evaporated onto the substrate Co or Ni and/or oxygen compounds thereof and/or alloys formed of these elements.

To obtain predetermined optical properties of the coating one or more elements of the group of the rare earths, and/or elements of this group together with oxygen compounds thereof, and/or elements of this group and compounds thereof with group VII of the Periodic System, and/or the elements Al, Au, Be, Co, Cu, In, Mg, Mn, Mo, Nd, Ni, Pb, Sb, Ta, Th, W, Y, Zn, and Zr, and/or oxygen compounds and/or compounds thereof with group VII of the Periodic System and/or compounds of the aforesaid elements may be evaporated onto the substrate.

To obtain predetermined radioactive properties of the coating one or more of the following elements may be evaporated onto the substrate Ac, Am, At, Cf, Cm, Es, Fm, Fr, Md, Np, No, Pn, Po, Pm, Pa, Ra, Rn, and Tc.

To obtain predetermined photoelectric properties of the coating one or more of the following elements may be evaporated onto the substrate Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cs, Cu, Ga, Ge, In, K, La, Li, Mg, Mn, Mo, Pb, Pd, Rb, Re, Rh, Sb, Si, Sn, Sr, Ta, Te, Th, Te, V, W, Zn and Zr and/or compounds of these elements with group VII of the Periodic System.

To obtain predetermined semiconductive properties of the coating one or more of the following elements may be evaporated onto the substrate germanium, or silicon, or III/V compounds or II/VI compounds thereof.

As will be readily apparent to the one skilled in the art a coating simultaneously possess two or more physical characteristics. To produce a coating having simultaneously a certain electrical conductivity and magnetic properties one or several of the following elements, are accordingly evaporated onto the substrate Al, Au, Be, Cd, Co, Cu, In, Mg, Mu, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Sm, Sn, Sr, Ta, Th, Tl, Tm, Vb, Y, Yb, Zn and Zr and/or oxygen compounds of one or more of these elements whereby the oxygen compound deposited on the substrate is of a lower degree of oxidation than the substance employed, and/or alloys formed of the above elements, together with one or more of the elements Co or Ni and/or oxygen compounds thereof and/or alloys formed of these elements.

In a similar manner, a coating may have both the property of certain electrical conductivity as well as certain optical properties. In this case one or more of the following elements may be evaporated onto the substrate Al, Au, Be, Cd, Co, Cu, In, Mg, Mu, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Sm, Sn, Sr, Ta, Th, Tl, Tm, V, W, Y, Yb, Zn and/or oxygen compounds of one or more of these elements whereby the oxygen compound deposited on the substrate is of a lower degree of oxidation than the substance employed, and/or alloys formed of the above elements, as well as one or more of the elements of the group of the rare earths, and/or elements of this group together with oxygen compounds thereof, and/or elements of this group and compounds thereof with group VII of the Periodic System, and/or the elements Al, Au, Be, Co, Cu, In, Mg, Mn, Mo, Nd, Ni, Pb, Sb, Ta, Th, W, Y, Zn and Zr and/or oxygen compounds and/or compounds thereof with group VII of the Periodic System and/or compounds of the aforesaid elements.

When evaporating onto the substrate for example the elements aluminium or gold in order to obtain a predetermined electrical conductivity of the coating it will be readily apparent to the one skilled in the art that the optical properties are likewise modified in a certain manner. By suitable selection of the concentration of the physically active materials a specified electrical conductivity of the coating may be obtained wherein the coating simultaneously has specified optical properties such as reflectivity or transmission. Additionally, the optical transmission may be altered by adding dyes.

By appropriate selection of physically active materials predetermined values of the various physical properties of electrical conductivity, magnetic properties, optical properties, radioactive properties, photoconductive properties

and semiconductive properties may be combined in any desired combination in one and the same coating.

Coatings produced by the method of the present invention may serve the most varied uses so that only some fields of application may be mentioned here for illustrative purposes. By combination of the quartz and the metal boride and/or metal silicide with an electrically conductive material resistors or capacitors may be produced. By combining various physical properties the coatings may find application in the art of electrical heat generation and for removing electrostatic surface charges. The combination of optical, photo-conductive and semiconductive properties may be employed in the field of semiconductor technology. The invention will be described in more detail in the following examples.

Example 1

Five parts by weight of quartz were added to one part by weight of tungsten boride and to one part by weight of Ni as a substance with magnetic properties and the vaporizable mixture thus obtained was heated under a high vacuum to a temperature of about 1300°C, in a molybdenum crucible. This mixture was readily converted into the vapor phase and the vapor was deposited on a carrier plate in a high vacuum.

Example 2

Five parts by weight of quartz were added to one part by weight of tungsten boride and to two parts by weight of properties, for example Co as a substance with optical properties and the vaporizable mixture thus obtained was heated under a high vacuum to a temperature of about 1300°C, in a molybdenum crucible. The mixture was readily converted into the vapor phase and the vapor was deposited on manufactured and ground lenses in a high vacuum.

The degree of absorption was constantly measured by a photometer and evaporation was discontinued as soon as the required degree of absorption was obtained.

Residues were readily removed from the crucible after completion of the evaporation process. The crucible was undamaged and was re-used repeatedly. The thickness of the film applied on the lenses was 1.5 μ. The lenses had a slightly blue color and were free of any colored reflections; they are, suitable as protection for sensitive eyes.

The lenses, which were rotated above the crucible during the evaporation process, had a completely uniform transparency free from any, streaks over their entire surface. The film applied by evaporation had a thickness of 1,5 μ. It was free of disturbing interference phenomena and ready for use without any repolishing. The film is scratchproof in use. The coated lenses were subjected to known after treatment (annealing) at 400°C for one hour and then had a pleasant blue transparent color. Residues were readily removed from the crucible.

Example 3

The evaporation method according to examples 1 or 2 was performed in two separate crucibles, one of which contained the carrier substance and the other one the evaporated substance with the magnetic conductivity or optical properties. The proportions of the carrier material and tungsten boride and the evaporated substance in the mixture were found to be very favorable.

Example 4

Five parts by weight of quartz were added to one part by weight of tungsten boride and to one part by weight of Ac as a substance with radioactive properties and the vaporizable mixture thus obtained was heated under a high vacuum to a temperature of about 1300°C, in a molybdenum crucible. The mixture was readily converted into the vapor phase and the vapor was deposited on a carrier plate in a high vacuum.

Example 5

Five parts by weight of quartz were added to one part by weight of tungsten boride and to one part by weight of Be as a substance with photoelectric properties and the vaporizable mixture thus obtained was heated under a high vacuum to a temperature of about 1300°C, in a molybdenum crucible. The mixture was readily converted into the vapor phase and the vapor was deposited on a carrier plate in a high vacuum.

Example 6

Five parts by weight of quartz were added to one part by weight of tungsten boride and to one part by weight of germanium oxide as a substance with semiconductive properties and the vaporizable mixture thus obtained was heated under a high vacuum to a temperature of about 1300°C, in a molybdenum crucible. The mixture as readily converted into the vapor phase and the vapor was deposited on a carrier plate in a high vacuum.

Example 7

Examples 1—6 were repeated, but the tungsten boride was replaced by a metal silicide, for example tungsten silicide.

WHAT I CLAIM IS:—

1. A method of producing coatings by vacuum deposition which method comprises evaporating onto a substrate a carrier material which comprises quartz and a metal boride and/or a metal silicide simultaneously with at least one of the elements Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cs, Cu, Dy, Er, Eu,

Ga, Gd, Ge, Ho, K, La, Li, Lu, In, Ma, Mn, Mu, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Tl, Tm, V, W, Y, Yb, Zn, Zr, Ac, Am, Ae, Bc, Cf, Cm, Es, Fm, Fr, Md, Np, No, Pn, Po, Pm, Pa, Ra, Rn or Tc or compounds of the said elements, or alloys formed from the above elements.

2. A method as claimed in claim 1 which comprises evaporating onto the substrate one or more of the folloing elements Al, Au, Be, Cd, Co, Cu, In, Mg, Mu, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Sm, Sn, Sr, Ta, Th, Tl, Tm, V, W, Y, Yb, Zn or Zr and/or an oxygen compound of one or more of these elements and/or alloy formed from the said elements in order to obtain a predetermined electrical conductivity of the coating.

3. A method as claimed in claim 1 or claim 2 which comprises evaporating onto the substrate one or both of the elements Co or Ni and/or oxygen compounds thereof and/or alloys formed from these elements in order to obtain predetermined magnetic properties of the coating.

4. A method as claimed in any one of the preceding claims which comprises evaporating onto the substrate one or more elements of the group of the rare earths, Al, Au, Be, Co, Cu, In, Mg, Mn, Mo, Nd, Ni, Pb, Sb, Ta, Th, W, Y, Zn or Zr, and/or oxygen compounds and/or compounds thereof with group VII of the Periodic System and/or compounds of the said elements in order to obtain predetermined optical properties of the coating.

5. A method as claimed in any one of the preceding claims which comprises evaporating onto the substrate one or more of the elements Ac, Am, At, Bc, Cf, Cm, Es, Fm, Fr, Md, Np, No, Pn, Po, Pm, Pa, Ra, Rn or Tc in order to obtain predetermined radioactive properties of the coating.

6. A method as claimed in any one of the preceding claims which comprises evaporating onto the substrate one or more of the elements Al, As, Au, Ba, Be, Bi, Ca, Cd, Ce, Co, Cs, Cu, Ga, Ge, In, K, La, Li, Mg, Mn, Mo, Pb, Pd, Rb, Re, Rh, Sb, Si, Sn, Sr, Ta, Te, Th, V, W, Zn or Zr and/or compounds of these elements with group VII of the Periodic System in order to otbain predetermined photoelectric properties of the coating.

7. A method as claimed in any one of the preceding claims which comprises evaporating onto the substrate one or more of the elements germanium or silicon or III/V compounds or II/VI compounds thereof, in order to obtain predetermined semiconductive properties of the coating.

8. A method as claimed in any one of the preceding claims wherein the metal boride or silicide is tungsten boride or silicide.

9. Vacuum deposited coating whenever produced by the method as claimed in any one of the preceding claims.

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